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Superconductivity and Eu Valence Instability in Undoped Eu3Bi2S4F4[1] HUI-FEI ZHAI, PAN ZHANG, GUANG-HAN CAO, Department of Physics, Zhejiang University, Hangzhou 310027, P. R. China — We recently synthesized a novel bismuth sulfofluoride, $EuBiSF^2$,[1] a CDW-like transition occurs at 280 K, below which SC emerges at 0.3 K. The Eu ions show an anomalously mixed valence about +2.2. With structural design, we successfully synthesized a new europium bismuth sulfofluoride, $Eu^3Bi^2S^4F^4$.[2] The compound crystallizes in a tetragonal lattice (space group I4/mmm, a = 4.0771(1) Å, c = 32.4330(6) Å, and Z = 2), in which CaF^2-type Eu^3F^4 layers and NaCl-like BiS^2 bilayers stack alternately along the crystallographic caxis. There are two crystallographically distinct Eu sites, Eu(1) and Eu(2) at the Wyckoff positions 4e and 2a, respectively. Our bond valence sum calculation, based on the refined structural data, indicates that Eu(1) is essentially divalent, while Eu(2) has an average valence of +2.64(5). This anomalous Eu valence state is further confirmed and supported, respectively, by Mössbauer and magnetization measurements. The Eu3+ components donate electrons into the conduction bands that are mainly composed of Bi 6px and 6py states. Consequently, the material itself shows metallic conduction and superconducts at 1.5 K without extrinsic chemical doping. [1] Hui-Fei Zhaiet al.,Phys. Rev. B90, 064518 (2014). [2] Hui-Fei Zhaiet al.. J. Am. Chem. Soc. 2014, 136, 15386 −15393.

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